OPTIMIZATION OF THE SCALED-UP COAXIAL-ELECTRODE COPPER IONIZATION CELL FOR WATER DISINFECTION

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Nissim Gore-Datar

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OPTIMIZATION OF THE SCALED-UP COAXIAL-ELECTRODE COPPER IONIZATION CELL FOR WATER DISINFECTION

Approved by:

Dr. Xing Xie, Advisor
School of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. Yongsheng Chen
School of Civil and Environmental Engineering
Georgia Institute of Technology

Dr. Sotira Yiacoumi
School of Civil and Environmental Engineering
Georgia Institute of Technology

Date Approved: December 2, 2020

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LIST OF ABBREVIATIONS

CECIC	Coaxial Electrode Copper Ionization Cell
CIC	Copper Ionization Cell
DBP	Disinfection By-Product
DI	Deionized
EPA	Environmental Protection Agency
HRT	Hydraulic Retention Time
LB	Luria-Bertani
LEEFT	Locally Enhanced Electric Field Treatment
LIE	Log Inactivation Efficiency
MCLG	Maximum Contaminant Level Goal
SEM	Scanning Electron Microscope
UV	Ultraviolet

SUMMARY

Over 800 million people worldwide lack access to clean, uncontaminated drinking water, and over 1.1 million people in America lack a piped water connection. The public health consequences of this issue have been worsened by the ongoing pandemic, which has made the availability of clean water for hand washing more important. Centralized solutions to this issue, such as chlorination or membrane filtration, are too costly and energy intensive for widespread application in the developing world, and sometimes even pose their own risks, such as the formation of carcinogenic disinfection by-products (DBPs). Point-of-use solutions such as chlorine tablets or UV disinfection are more practical, but can also be energy intensive and pose DBP risks. The coaxial-electrode copper ionization cell (CECIC) is a water disinfection system developed to fill this gap using the biocidal properties of copper aided by other mechanisms such as electrophoresis, strong localized electric fields, and in-situ generation of copper ions.

The CECIC has been proven to be highly effective (>6-log inactivation of *E. coli* with ~200 μg/l Cu) when tested with DI water at low flow rates in a reactor with an effective volume of 10 ml. In order to meet real-world conditions, it is necessary to scale up the system to a larger prototype and test its performance with more conductive waters at higher flow rates. This presents several challenges, such as maintaining a strong localized electric field with a low voltage in spite of the larger radius (inter-electrode distance) of the cell, keeping copper concentrations low in spite of a higher rate of copper release in more conductive water, and ensuring high bacterial inactivation in spite of a reduced hydraulic retention time (HRT). On the other hand, the larger cell of the scaled-up CECIC also allows for more flexibility with the anode configuration. More wires can be installed parallel to the flow and equidistant from the axis to reduce the gap between the electrodes,

in turn creating more regions with enhanced electric field strength. The anode can also be positioned at an angle to the flow so as to increase mixing and contact with bacteria.

Various experiments are designed and conducted in order to test these configurations and optimize the performance of the scaled-up CECIC under high-conductivity, high-flow conditions. Configurations consisting of 1, 3 and 6 wires positioned parallel to the flow as well as 3 wires positioned inclined to the flow are tested for their response to different flow rates (100 – 250 ml/min) at the same voltage (3 V) and to different voltages (0.5 – 7 V) at the same flow rate (150 ml/min). The results of these experiments show that inclining the wires reduces the disinfection performance rather than increasing it, but do not clearly indicate whether increasing the number of wires helps improve performance.

Further testing is carried out with the original configuration (1 coaxial wire) to ascertain the synergetic role played by the electric field and copper concentration gradients by controlling the current supplied to the cell. These experiments demonstrate that the synergetic effect does play an important role even in the scaled-up reactor, with the disinfection performance improving significantly as the electric field strength increased.

Lastly, the scaled-up system is tested with real water samples (river water and rain water) that are pre-treated to remove experimental interference from suspended solids and pre-existing microorganisms while preserving the real water matrix. Over 99% of bacteria are inactivated by the CECIC in both cases, with an effluent copper concentration of ~550 μg/l. This performance is lower than that achieved at the same conditions with synthetic water, likely due to interference from dissolved substances in the real water. However, this demonstrates that the scaled-up CECIC can disinfect real water samples too, which is an important stepping stone to pilot studies and field deployment.

CHAPTER 1
INTRODUCTION

Over 1.1 million people in America lack a piped water connection, with almost half of them located in big cities (Meehan et al, 2020). Far from improving, this 'plumbing poverty' is likely to stagnate or worsen in the future. The consequences of this are even more acute in context of the ongoing pandemic, which necessitates the availability of clean water for regular hand-washing and has introduced financial hardships that may limit the ability to purchase bottled water.

One solution to this problem is to provide to these households water from centralized treatment plants which rely on techniques such as ozonation, chlorination, ultraviolet disinfection and membrane filtration. However, some of these solutions are costly or energy intensive, while some pose their own risks, such as the release of lead from pipes into drinking water (Liu et. al, 2009) or the formation of carcinogenic disinfection by-products (DBPs) (Mitch and Sedlak, 2002), both of which can be caused by the chloramine that is added at plants to provide residual disinfection capacity to the water in the distribution system.

Providing water supply to such households presents a major challenge to water utilities around the country, but also provides the opportunity to leapfrog older piping systems and install 'smart' conveyance systems which provide added protection to the drinking water within the distribution system. An alternative to this could be point-of-use water treatment, a suite of technologies which can not only tackle this plumbing poverty in rich countries, but also cater to the over 800 million people worldwide who lack an uncontaminated drinking water source close to home (WHO 2017).

This thesis studies a unique device for point-of-use disinfection, called the Coaxial Electrode Copper Ionization Cell (CECIC), which can be configured as a smart conveyance system (if retrofitted or installed in distribution pipes) or as a point-of-use system (if installed in taps or water bottles). Chapter 2 provides a background on the biocidal properties of copper, its suitability for drinking water applications, and the constraints involved therein. It also provides an overview of the prior work done by the Xie group on CECIC and covers the hypotheses underlying the experiments conducted in this research. Chapter 3 details the experimental and analytical methods involved in testing those hypotheses, as well as the limitations of the techniques and equipment used. Chapter 4 discusses the outcomes of the experiments and their possible explanations. Chapter 5 concludes the thesis with a discussion of the implications of these findings as well as the further investigations needed before the CECIC can be scaled-up successfully.

CHAPTER 2

BACKGROUND

2.1 Copper Disinfection and its Advantages

Copper is an abundant, cheap metal with well-established biocidal properties that has been widely used for water purification. In its ionized form, copper can lead to the formation of free radicals that damage the cell membrane of bacterial cells, causing them to leak intracellular solutes and take up the copper ions, which then react with intracellular substances like proteins and nucleic acids substances (Borkow and Gabbay, 2005). This leads to inactivation of the bacterial cell and disinfection of the water.

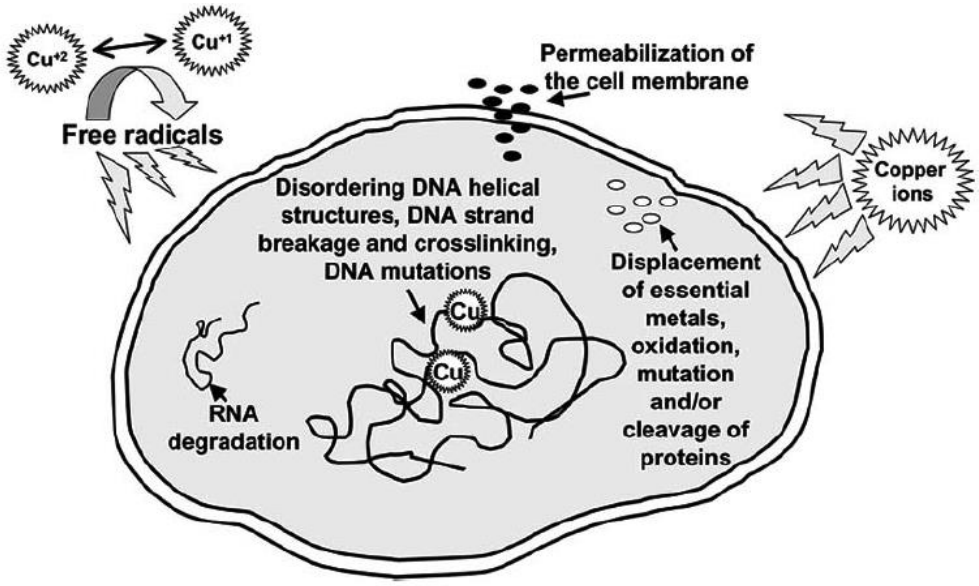

Figure 2.1: Mechanisms by which copper affects microorganisms. Adapted from Borkow and Gabbay, 2005.

Though it is such an effective biocide even at low dosages, copper is far less toxic to mammals at the same dosage (Flemming and Trevors, 1989), and is in fact an essential trace element for humans (Tapiero et al, 2003), with an intake of 8-10 mg/day being considered tolerable for adults. This difference between the concentrations at which it is toxic to microbes and humans respectively makes it a potential candidate for use in drinking water disinfection so long as its release can be controlled.

Copper also has several advantages compared to chlorine, which is the most widely used water disinfectant in the United States (Gordon et al., 1988). Being a solid, copper is both denser and far more stable than chlorine, which makes it safer and easier to store and transport. Moreover, copper disinfection does not generate carcinogenic DBPs as chlorination does, thereby minimizing additional risk to the consumer so long as the copper concentration is within the maximum contaminant limit goal (MCLG) of 1300 μg/l (USEPA, 2009).

Recently, studies have confirmed the biocidal effects of copper in the form of a variety of nanoparticles, from copper oxide nanoparticles (Meghana et al., 2015) to zeolite-rich copper solids (Rossainz-Castro et al., 2016), though the remaining concentrations of copper may limit their use in drinking water applications. Copper ionization cells (CICs) represent another emerging tool for copper-based disinfection, utilizing in-situ generation of copper. In its planar form, the CIC consists of 2 planar electrodes facing each other, which leads to in-situ copper release and the formation of a uniform electric field between the electrodes when a voltage is applied (Triantafyllidou et al., 2016). These planar cells with copper-silver ionization have been used in controlling biofilm- and plankton-associated waterborne pathogens, with copper concentrations of 400 – 800 μg/l (alongside silver ions of 40 – 80 μg/l) resulting in complete inactivation of biofilm-associated pathogens such as *Acinetobacter baumannii* (Shih and Lin, 2010). Copper-silver

ionization has also been used for *Legionella* control in water distribution systems of hospitals and is regarded the best available technology for that application (Lin et al., 2011). More recently, CICs have been demonstrated to be capable of microalgae inactivation of up to 98.5% with a relatively low effluent copper concentration of ~500 μg/l (Liu et al, 2020).

2.2 CECIC: Principles and Mechanisms

The coaxial-electrode copper ionization cell (CECIC) is a copper-based disinfection technology designed to enable high disinfection performance while releasing low concentrations of copper into the water being treated (Zhou et al, 2019). Compared with a planar CIC, the CECIC showed higher disinfection with lower copper release under the same operation parameters (Zhou et al, 2019). This is achieved by a combination of mechanisms that supplement the biocidal properties of copper, allowing it to be effective in killing pathogens even at concentrations low enough to not pose a risk to human bodies.

The coaxial configuration of the electrodes leads to a non-uniform electric field being generated within the cell. This field is particularly strong near the center electrode, causing an increase in the permeability of the cell membrane, thereby making the bacteria more susceptible to copper ion uptake and inactivation (Zhou et al, 2019). Moreover, the forces of electrophoresis and dielectrophoresis drive the bacterial cells (negatively charged in the case of gram-negative bacteria such as *E. coli*) towards the center electrode (anode), where the copper concentration is also higher due to the in-situ ionization of the copper (Zhou et al, 2019). This leads to a synergy between the strong electric field and the high localized copper ion concentrations, which allows for high disinfection performance with even a low concentration of copper.

2.3 Original CECIC Prototype and Results

The first prototype of the CECIC, as seen in Figure 2.2, consists of a cylindrical reactor made of acrylic, which contains a copper shim covering its inner surface and a copper wire suspended along its axis. The shim (McMaster-Carr, thickness 152 μm) acts as the negative electrode (cathode) while the wire acts as the positive electrode (anode). The reactor is held in place by 2 acrylic blocks which contain inlet and outlet ports for the connection of tubes, and removable panels through which the anode wire can be replaced. The anode wire is made of copper (McMaster-Carr, 110 copper wire) and has a diameter of 78 μm. It is held taut by tightly screwing on the removable panels on the acrylic block so as to maintain its coaxial position. This ensures a uniform electric field cross-section across the entire length of the reactor and minimizes chances of a short circuit. With a length of 13.8 cm and an inner diameter of 0.95 cm, this CECIC prototype has an effective volume of 10 ml.

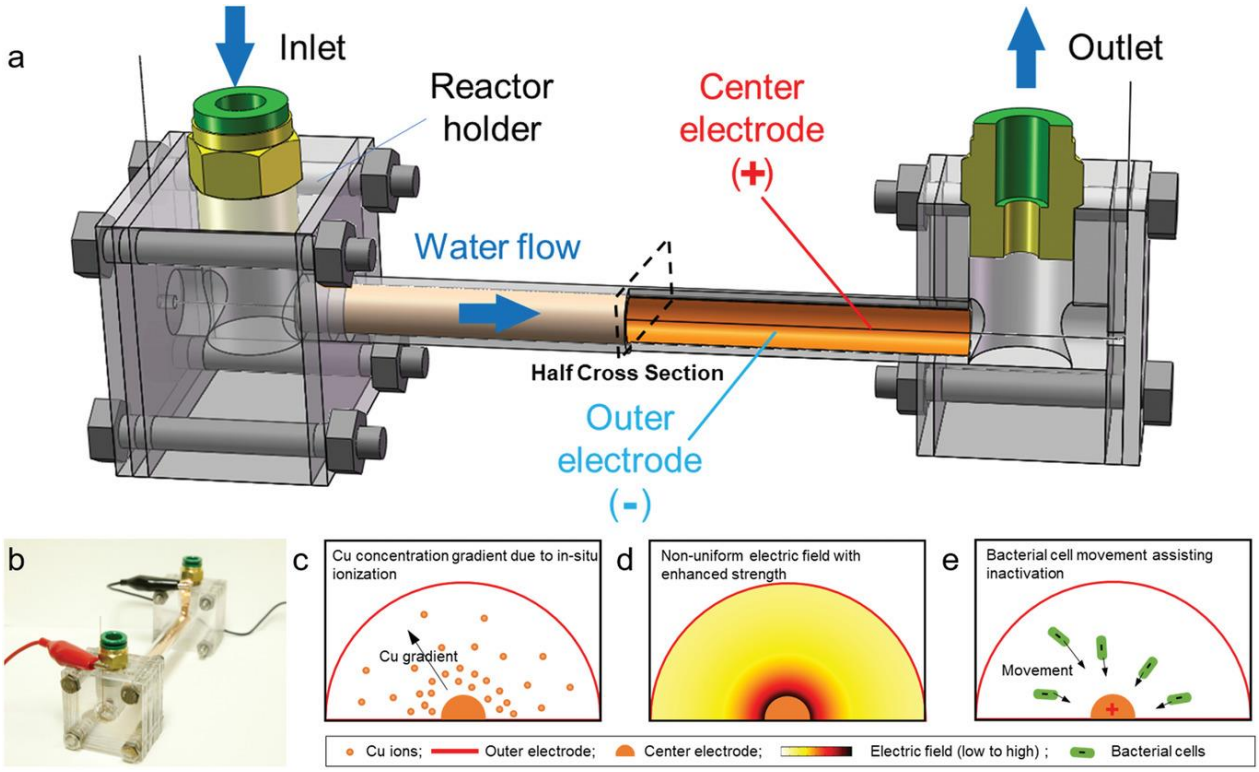

Figure 2.2: 10 ml CECIC: (a) 3D model showing components of the reactor, (b) photo of experimental setup and (c), (d), (e) schematic showing disinfection mechanisms. Adapted from Ding et al., 2019.

This prototype has been used to understand the aforementioned mechanisms and successfully produce over 6-log inactivation of *E. coli* in DI water with just 200 µg/l of Cu ions released into the water (Zhou et al, 2019). The device has also been shown to be compatible with portable power sources such as hand-held triboelectric nanogenerators (Ding et al., 2019) and smartphones, maintaining its high inactivation efficiency and low copper release even on being tested on synthetic waters with varying salt concentrations (Zhou et al, 2020B).

These results with the original prototype provided a strong proof-of-concept for the CECIC technology. However, most of these tests represented ideal conditions, wherein both the conductivity and flow rates of the water were low. The small diameter of the cell enabled the

generation of a strong electric field (>80 V/cm at the surface of the anode) with even a small voltage like 1.5 V (Zhou et al, 2019). The low conductivity of the DI water meant that the rate of copper release (which is proportional to the current drawn) at 1.5 V was low enough to remain below EPA limits even at a low flow rate of 2 ml/min.

2.4 Electrode Modification for Electric Field Enhancement

Early in this research, anode surface modification was investigated as a possible method of enhancing the performance of the CECIC. This was inspired by prior research done by the group, wherein copper oxide nanowire-modified electrodes had been successfully used for water disinfection by locally enhanced electric field treatment (LEEFT). This method uses nanowires grown perpendicular to the coaxial anode surface to produce another level of electric field enhancement by utilizing the 'lightning rod effect', which in turn produces a localized field strong enough for low-voltage bacterial electroporation (Zhou et al, 2020A).

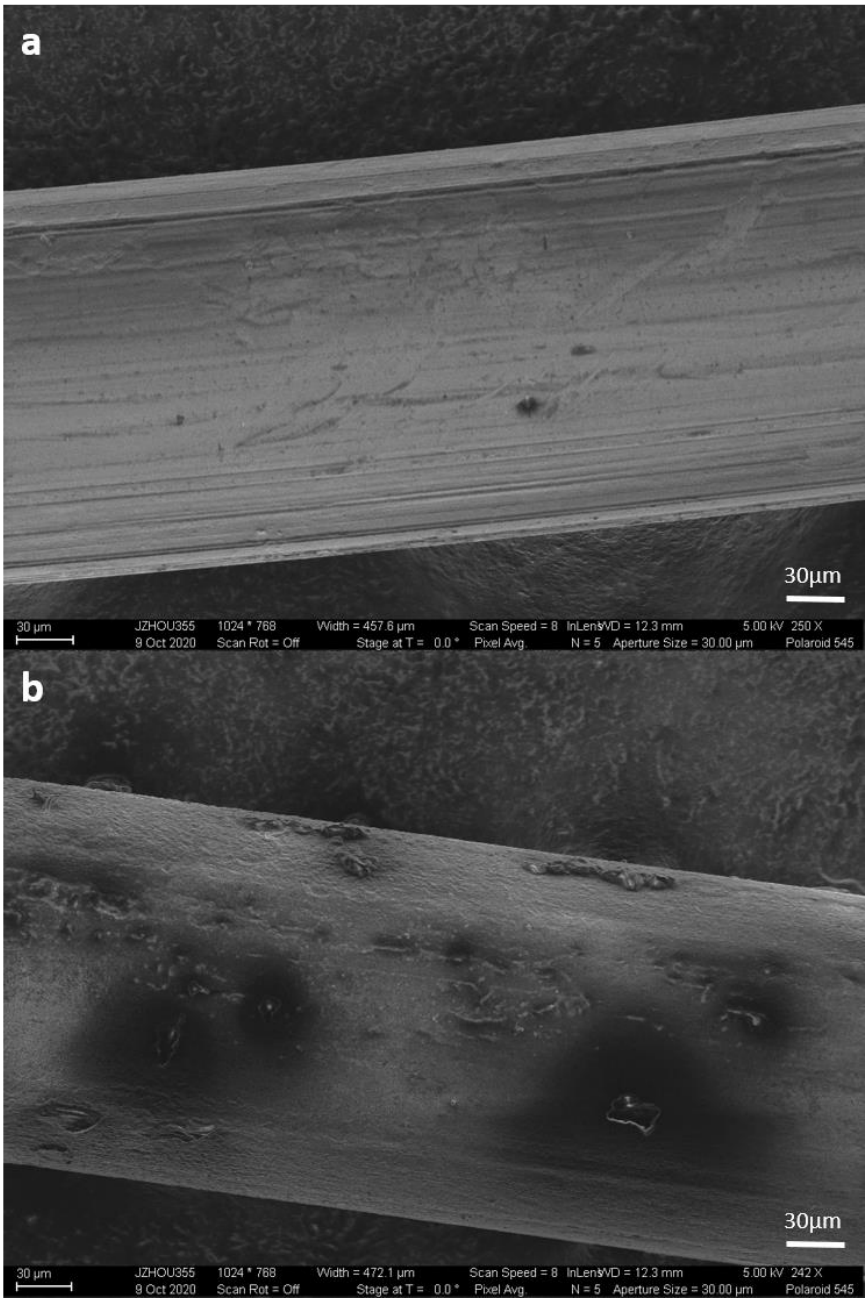

Figure 2.3: SEM images (Zeiss Ultra60) showing 201 µm-diameter copper wires (a) before and (b) after etching.

In order to create surface features such as grooves and peaks, an etching solution was produced based on a recipe developed by Wei et al. (2012) and the copper wire was immersed in it for different durations. As can be seen in Figure 2.3, the etching process resulted in a uniform

reduction of the wire diameter and the formation of a few surface features, but the desired surface morphology was not achieved. Hence this line of investigation was suspended after preliminary tests and the focus was shifted to optimization of the larger CECIC.

2.5 Scaling up

Since the system is intended for application to water distribution systems or bottle-sized portable POU systems, it was important to scale-up to a larger reactor that more accurately represented these real-world conditions. With that in mind, a larger prototype with an effective volume of 90 ml was developed and tested with synthetic and real waters (50 - 100 µS/cm) at higher flow rates (100 - 250 ml/min).

The scaled-up CECIC is a larger cell with an internal diameter of 3 cm, length 13 cm and effective volume 90 ml. With a diameter similar to some household pipes, this cell is an important stepping stone to pilot testing and eventual deployment, which is intended for household pipes, 'smart' water bottles and municipal drinking water distribution systems, which have an even larger pipe diameter. The main challenges in bringing the CECIC system closer to real-world conditions are increasing the size of the cell and the flow rate of the water, and preserving the electric field effect in more conductive water.

The following equation (Di Bartolo, 2004) governs the electric field distribution on a cross-section of a coaxial electrode system:

$$E_s = \frac{U}{s \cdot ln\left(\frac{R_c}{R_o}\right)}$$

where E_s is the strength of the electric field at a distance of s from the axis (anode), U is the voltage applied across the electrodes, R_c is the radius of the center electrode (wire radius), and Ro is the radius of the outer electrode (pipe radius). As R_o increases, the electric field strength decreases at a given distance from the axis for the same applied voltage. Thus the larger radius of the scaled-up CECIC would mean that a higher voltage is required to produce the electric field strength that was achieved in the original smaller cell. On the other hand, real waters have higher conductivity than DI water, due to which the same voltage applied to the CECIC produces a higher current, and hence a higher copper release, for real water than for DI water. This presents a challenge in experimental design and practical application since the electric field effect must be maximized while keeping copper concentrations within EPA drinking water limits of 1300 µg/l (USEPA, 2009).

CHAPTER 3

MATERIALS AND METHODS

These experiments involved a variety of analytical tools ranging from a pH meter to an Atomic Absorption Spectrometer. Properties such as pH and conductivity were measured before each experiment to understand the properties of the water being treated so that results could be benchmarked accordingly, or to verify that synthetic waters were correctly prepared. Properties such as log removal efficiency and copper concentration were the core indicators of system performance and were measured after each experiment.

3.1 Chemicals and Supplies

The chemicals and supplies listed in Table 3.1 were used for the various experiments and associated analytical processes.

Table 3.1: Chemicals and supplies, with their sources.

Material	**Specifications/Source**
Copper standard	1000 ± 3 µg/ml, 2% HNO_3, High Purity Standards
Copper wire	40AWG, Arcor bare copper wire
Brass pipe	12.7 cm (l) x 2.66 cm (d); McMaster-Carr
Nitric acid	70%, ≥99.999% trace metals basis, Sigma-Aldrich
Sodium sulfate	Anhydrous, ACS, VWR Amresco
Deionized water	Thermo Scientific Barnstead NanoPure

Table 3.1 continued: Chemicals and supplies, with their sources

Material	**Specifications/Source**
LB Broth, Miller	BD Difco
LB Agar, Miller	Culgene

3.2 Assembly of The CECIC

The body of the scaled-up CECIC consists of a brass pipe that doubles as the cathode. It has an internal diameter of 2.66 cm, length 13 cm and effective volume 90 ml. As seen in Figure 3.1, The cell is held in place by PVC fittings which contain ports for the connection of inlet and outlet tubes, and are closed off by 2 removable cap fittings. One of these caps contains a PDMS sealing plug through which the anode wire enters the cell. The other cap has a transparent acrylic window. The cell also contains a removable scaffolding on which the copper wire can be loaded in multiple configurations, as shown in Figure 3.1 (b) and Figure 3.2. The overall volume of the setup, inclusive of the fittings and the tubes, is ~150 ml. This whole setup is supported by a 3D-printed base made of ploylactic acid.

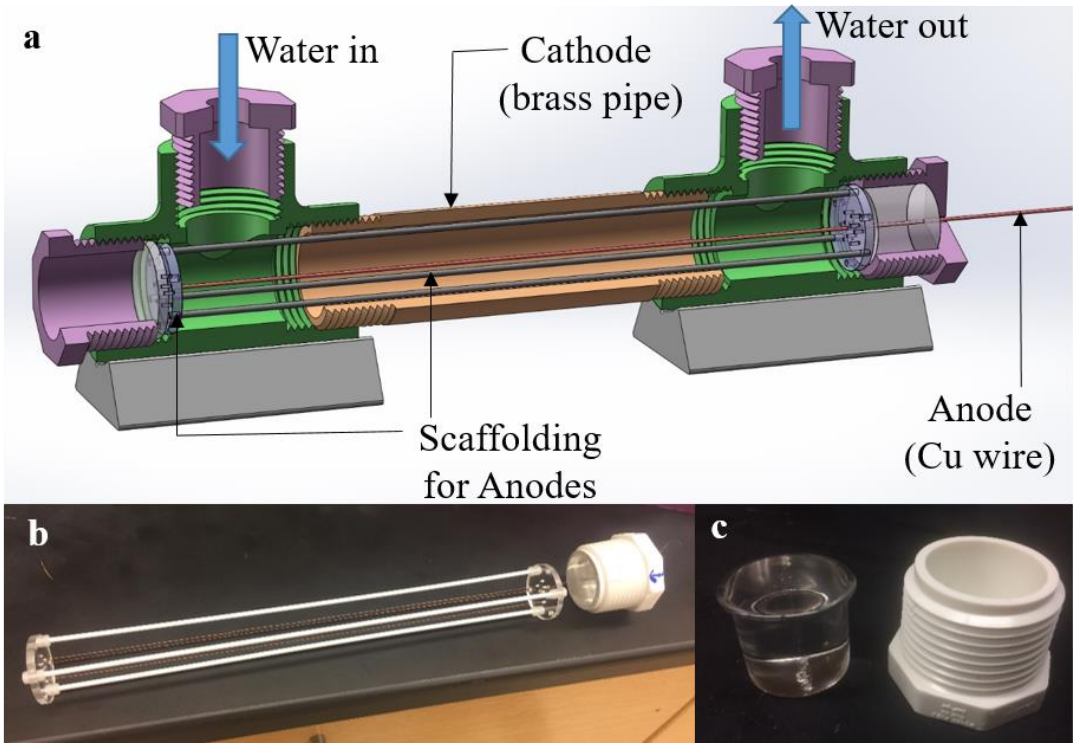

Figure 3.1: (a) 3D model showing components of the scaled-up CECIC reactor; (b) scaffolding, anode wires and cap; (c) PDMS plug and PVC cap (model and images: Beichen Lin).

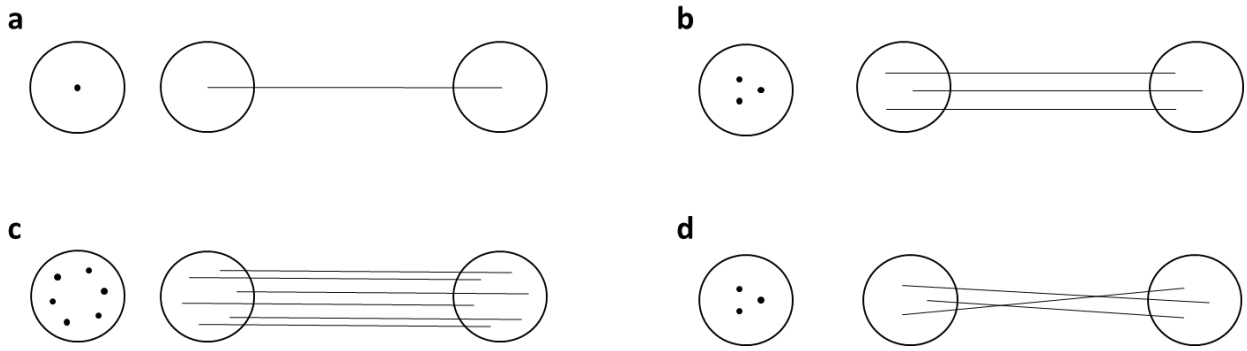

Figure 3.2: Schematics showing the arrangement of anode wires in (a) 1-wire, (b) 3-wire, (c) 6-wire and (d) 3-inclined-wire configurations. The distance of each wire from the pipe axis is 2.5 mm for the 3-wire configuration and 5 mm for the 6-wire configuration.

3.3 Water Sample Preparation

3.3.1 Synthetic Water Preparation

Synthetic water was prepared by adding Na_2SO_4 to DI water to create a 0.33 mM solution, which had a conductivity of 90-100 µS/cm. This conductivity was selected to be similar to the conductivity of Chattahoochee River water, as sampled near Atlanta (~92 µS/cm), which is also well within the range of conductivities of rivers in the US (50-1500 µS/cm) as documented by EPA (USEPA 2012). Na_2SO_4 was used so that the conductivity could be modified without affecting the pH of the distilled water, and without adding ions such as Cl^- (which would be the case with NaCl addition) that could contribute to disinfection upon oxidation and interfere with the results.

3.3.2 Real Water Collection and Pre-treatment

Real water samples were procured from 3 different sources:

1. Chattahoochee River: Water was collected from the surface of the flowing river at a point close to the shore in the Cochran Shoals area (33°54'13.5"N 84°26'41.4"W), near Atlanta on 9/2/2020.

2. Rain: Water was collected in a clean tray placed open to the sky outside the Ford Environmental Science & Technology building (33°47'20.4"N 84°23'40.4"W) during a storm on 9/17/2020.

3. Lake Lanier: Water was obtained from the intake of the Shoal Creek Filter Plant on the shores of Lake Lanier on 10/9/20.

All real water samples were stored in 5-gallon HDPE Carboys (McMaster-Carr) at 4^{o}C. Before the experiment, each sample was pre-treated: filtered using a 5µm filter paper (VWR

qualitative, 413), then autoclaved at 121°C & 20 psi for 20 minutes. This was meant to remove interference from pre-existing microorganisms and large suspended solids while preserving the matrix of dissolved ions and compounds.

3.4 Water Disinfection Experiments

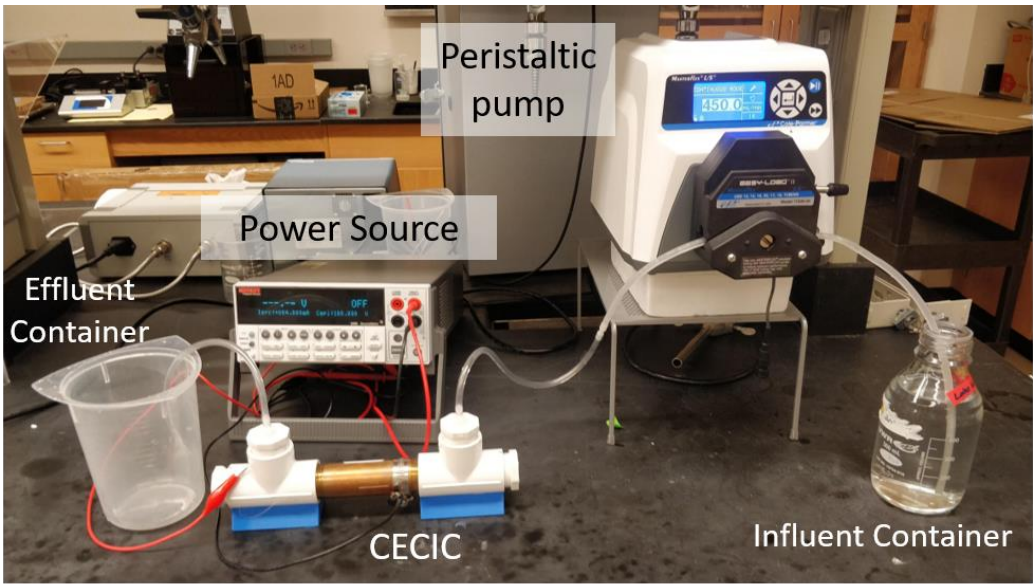

Figure 3.3: Experimental setup for water disinfection experiments with scaled-up CECIC.

In order to understand the effect of voltage, flow rate, and various anode configurations on the scaled-up CECIC, experiments were carried out by varying each of these parameters in turn. All of these experiments were carried out as follows: (1) The CECIC was assembled with the selected anode configuration and connected to the power source and peristaltic pump as shown in Figure 3.3. Synthetic water was pumped into the cell till it was filled. (2) Then the pump and power source were set to the selected values and switched on simultaneously. (3) Effluent samples (10-15 ml) were collected in metal-free centrifuge tubes (Labcon) after 360 ml of influent had flowed through

the cell in order to ensure steady-state conditions. (4) Current drawn by the cell as measured by the power source was noted at the time of effluent sample collection in order to calculate theoretical copper release and coulombic efficiency of the cell.

The voltage and/or flow rate were then modified as needed, and steps (2)-(4) were repeated for each new experiment within one batch (0.5, 1, 3, 5, or 7 V at 150 ml/min for voltage response experiments, and 100, 150, 200, or 250 ml/min at 3 V for flow rate response experiments). At the end of each such batch, the cell was emptied and disassembled, then dried using compressed nitrogen and tissue paper, then reassembled in the new configuration for another batch of experiments starting at step (1).

The concentrations of bacteria in each sample were evaluated by spread plating the samples 2-3 hours after collection. An influent sample was also collected once during each batch of experiments and plated along with the effluent samples to control for any bacteria that may have been inactivated in the time interval.

A power source (Kiethley 2400 SourceMeter) was used to supply DC voltage across the electrodes. It was used in both constant-voltage mode, wherein the voltage was set to a constant value and the current drawn at that voltage was displayed in real-time by the power source, and constant-current mode, wherein the current was set to a constant value and display showed in real-time the voltage applied to maintain that current.

3.5 Characterization

3.5.1 pH & Conductivity

pH and conductivity of all influent samples were measured immediately before each experiment using an Advanced Electrochemistry Meter (Thermo Scientific - Orion VersaStar Pro). pH was measured using a pH/ATC triode probe (Orion 8157BNUMD), and conductivity using a conductivity probe (Orion 013005MD).

3.5.2 Disinfection Efficiency

E. coli (ATCC 10798^{TM}) were used as the model bacteria in all the experiments. They were cultured aerobically in LB broth (obtained from Difco^{TM}) at 35^{o}C for 12-18 hours, being placed in a shaker set to 200 rpm. If required, this culture was stored at 4^{o}C for up to 7 days before being used for an experiment.

The bacteria were then harvested from the broth by centrifugation at 5000 rpm for 5 min (Beckman-Coulter Avanti J-E centrifuge) and washed 1-2 times with DI water. This solution was then diluted with DI water (or the pre-treated real water in case of real water experiments) to a concentration of ~1 x 10^7 CFU/ml.

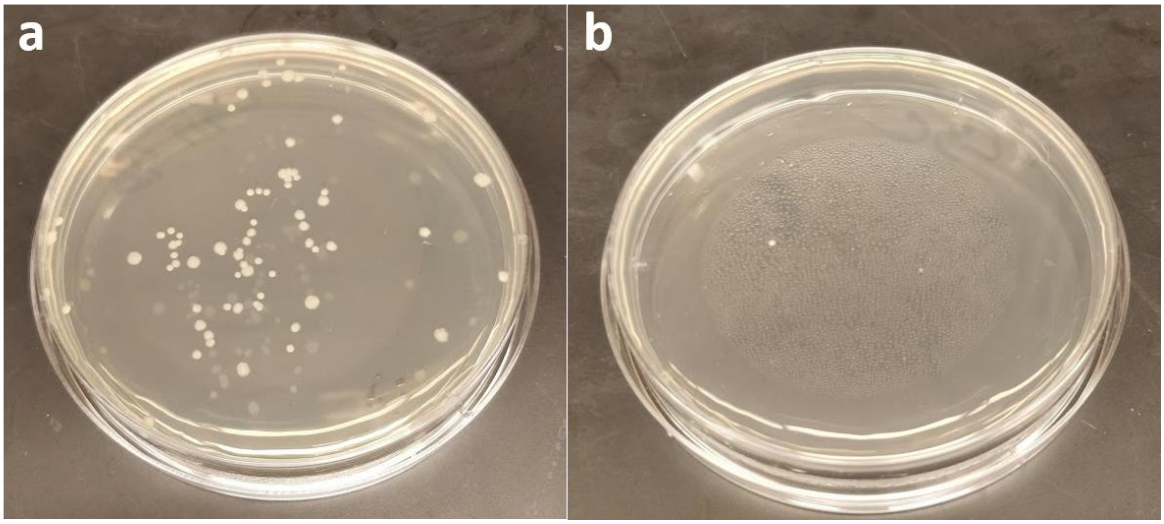

Figure 3.4: Agar plates with *E. coli* colonies from (a) lake water influent at 10^4x dilution and (b) CECIC-treated lake water effluent at 10^3x dilution, calculated to have 2.9-log inactivation.

Disinfection efficiency was measured using the spread-plate method. Each sample was diluted as required and plated in triplicate by spreading 100 µl of the sample on polystyrene petri dishes (VWR, 100 mm x 15 mm) containing LB agar obtained from BD Difco™. The plates were then stored at 35°C for 12-18 hours, following which the colonies, as seen in Figure 3.4, were counted manually. The original concentrations of bacteria in the samples, quantified as colony-forming units (CFU)/ml, were calculated by multiplying the colony count by the dilution factor and dividing this by the volume plated (i.e. 0.1 ml). In cases where multiple dilutions of the same sample were plated and the calculated concentrations were slightly different for different dilutions, the bacterial concentration of the less dilute sample was recorded.

After calculating the bacterial concentration of the influent (C_{inf}) and effluent (C_{eff}) for each experiment, the log inactivation efficiency (LIE) was calculated as follows:

$$\text{LIE} = -\log_{10}\left(\frac{C_{eff}}{C_{inf}}\right)$$

For triplicate samples, 3 LIEs were calculated – one for each C_{eff}, using the average of the influent concentrations as C_{inf} in each case – and their average and standard deviation were presented on the graphs.

3.5.3 Copper Concentration

To measure total copper concentration (Cu_{tot}), around 10 ml of the sample was acidified with HNO_3 to form a 2% (w/w) solution, and then was analyzed using an Atomic Absorption Spectrometer (PerkinElmer PinnAAcle 900F, with PerkinElmer S10 Autosampler). The AAS was calibrated before each set of measurements using standards prepared from copper solution. The calibration range used was 100 - 4000 µg/l (r^2 = 0.9995 – 0.9999), and samples with values below 100 µg/l were recorded as 0 µg/l due to the lack of accuracy at the low end of the calibrated range.

To measure the dissolved copper concentration (Cu_{dis}), another 5 ml of the sample was filtered using 0.45 µm syringe filters (VWR, 25 mm diameter) in order to remove the bacterial cells and any copper that may be bound to them. The filtered sample was then acidified and analyzed using the AAS in the same manner as the total copper. The copper taken up by the bacteria, thus causing their inactivation, is calculated as:

$$Cu_{bac} = Cu_{tot} - Cu_{dis}$$

For all copper concentrations, the standard deviations were under 2% and hence have not been included on the graphs.

CHAPTER 4
OPTIMIZATION OF THE SCALED-UP CECIC

4.1 Modelling of Electric Field Distribution

A 2-D electrostatic model was built on COMSOL to simulate the distribution of the electric field strength for various voltages and configurations of the scaled-up CECIC. This was done using the electrostatic module on COMSOL Multiphysics 5.5, with the electric field defined by the equation:

$$E = -\nabla V$$

where V is the electric potential.

As seen in Figure 4.1, these simulations showed that as the number of wires increased, the electric field strength increased at points closer to the edge of the cell but a ‘dead space’ with weak electric field was created around the axis of the cell. For each configuration, the electric field strength throughout the reactor increased as the voltage increased.

In order to study the effects of these competing factors (stronger field near the edge and weaker field along the axis), disinfection experiments were carried out with different anode configurations and at different voltages.

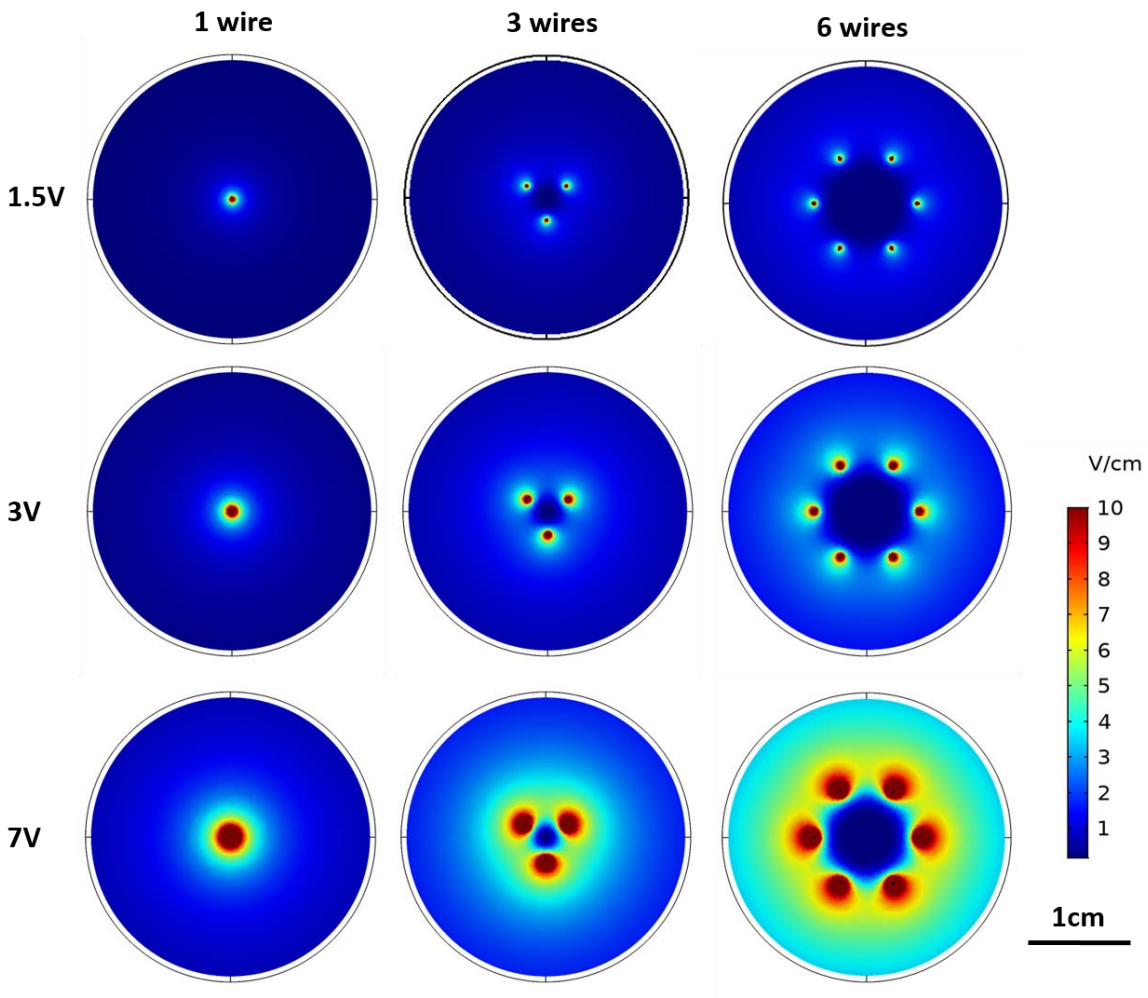

Figure 4.1: Electric field strength distribution for 1, 3, and 6 wire configurations at 1.5, 3, and 7 V.

4.2 Effect of Voltage on Scaled-up CECIC

Experiments were conducted to measure the effect of changes in voltage and anode configuration on the treatment efficiency of the scaled-up prototype, and to determine the optimal voltage at which a high disinfection efficiency can be achieved while meeting EPA standards. Each set of experiments was carried out the same flow rate of 150 ml/min (HRT = 36 s), while the constant voltage applied across the electrodes was varied in steps from 0.5 to 7 V. This was repeated with

4 different configurations of the anode: 1 coaxial wire, 3 equidistant wires parallel to the flow direction, 3 wires inclined with respect to the flow, and 6 equidistant wires parallel to the flow.

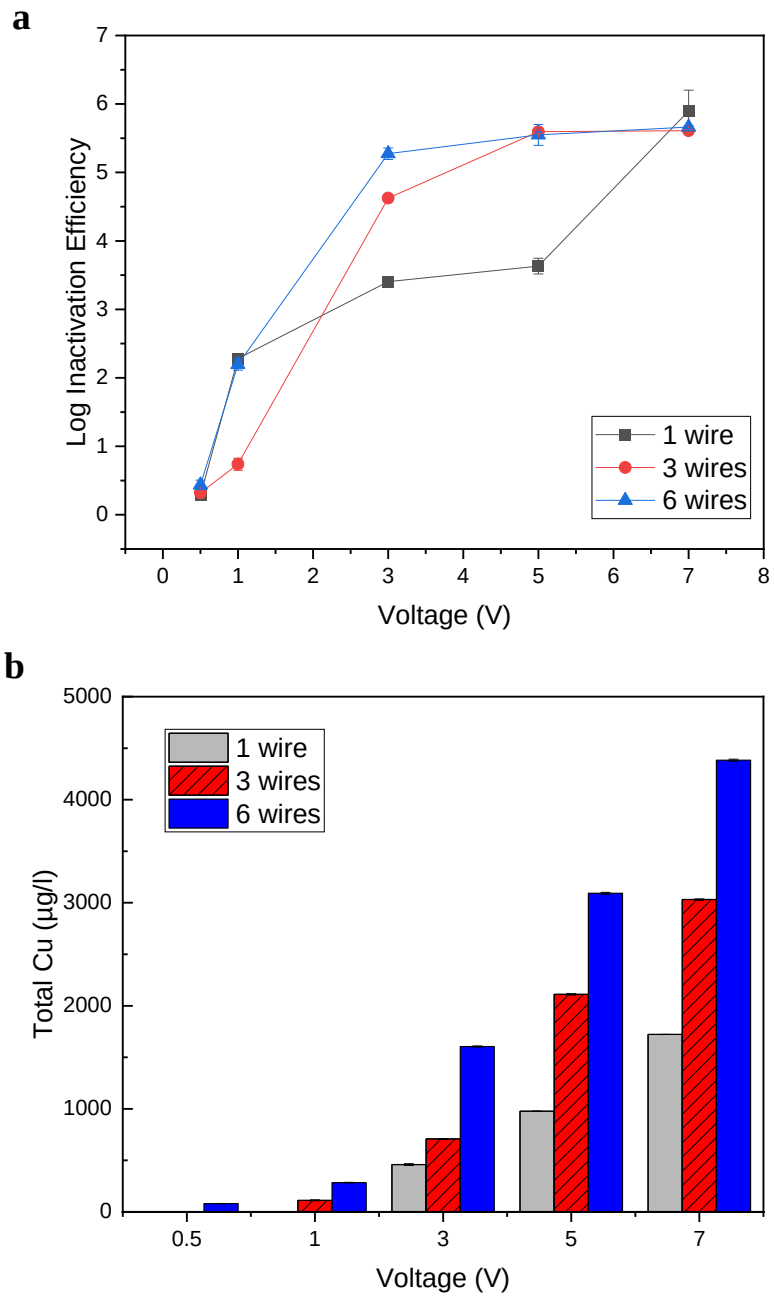

Figure 4.2: (a) LIE and (b) total copper for configurations with 1, 3 and 6 wires, at 0.5, 1, 3, 5 and 7 V, treating synthetic water at 150 ml/min.

As can be seen in Figure 4.2, the log inactivation for all configurations was similar at the lowest voltage, 0.5 V. This may be due to both low copper levels and a weak electric field. As the voltage increases (and with it the copper concentration), the differences in performance become more pronounced. At the highest voltage the values converge again as all configurations approach the maximum measurable log inactivation for this experimental design.

Based on these overall results, the highest disinfection efficiency of the CECIC while meeting EPA discharge limits at a flow rate of 150 ml/min is achieved with the 3 wire configuration at an operating voltage of 3 V. This configuration results in a 4.58-log inactivation of *E. coli* while releasing 700 µg/l of copper into the water, which is just over half of the EPA limit.

The inclined-wire configuration was intended allow more bacteria to come in contact with the anode, by providing a larger surface area relative to the direction of flow and by increasing mixing of the flow within the pipe. This in turn would increase the disinfection efficiency of the system. A comparison between the results for the 3-parallel and 3-inclined configurations can be seen in Figure 4.3:

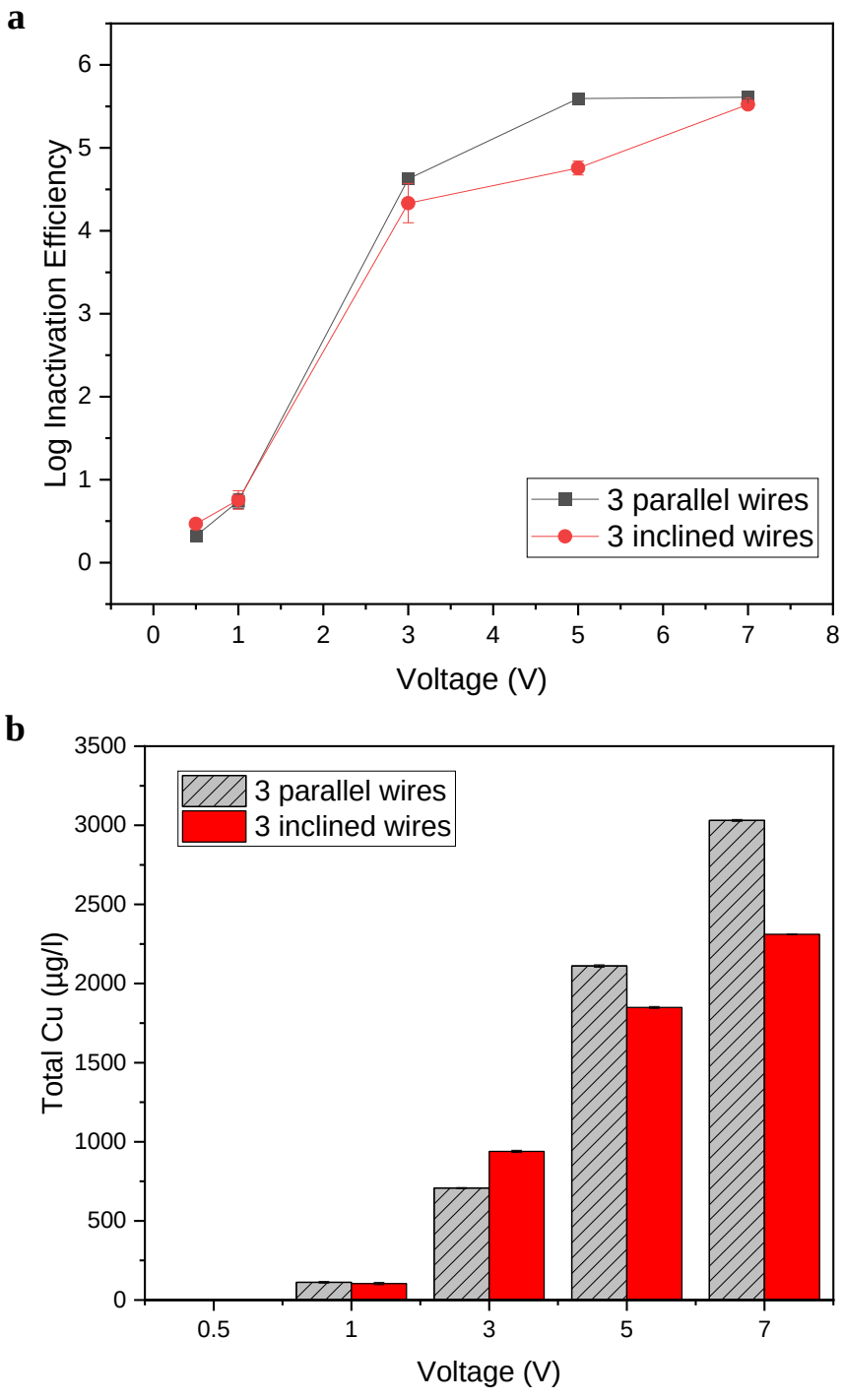

Figure 4.3: (a) LIE and (b) total copper for configurations with 3 straight wires and 3 inclined wires, at 3, 5 and 7 V, treating synthetic water at 150 ml/min.

Figure 4.3 suggests that the parallel-wire configuration is more effective than the inclined-wire configuration, with a higher LIE (4.58 v/s 4.35) at 3 V and (5.76 v/s 4.75) at 5 V. This difference is especially notable at 3 V since the straight wire configuration outperforms the inclined wire configuration in spite of releasing 24.6% less copper. Also worth noting is the fact that the percentage of released copper taken up by the bacteria is higher in the case of the parallel-wire configuration at 3, 5 and 7 V.

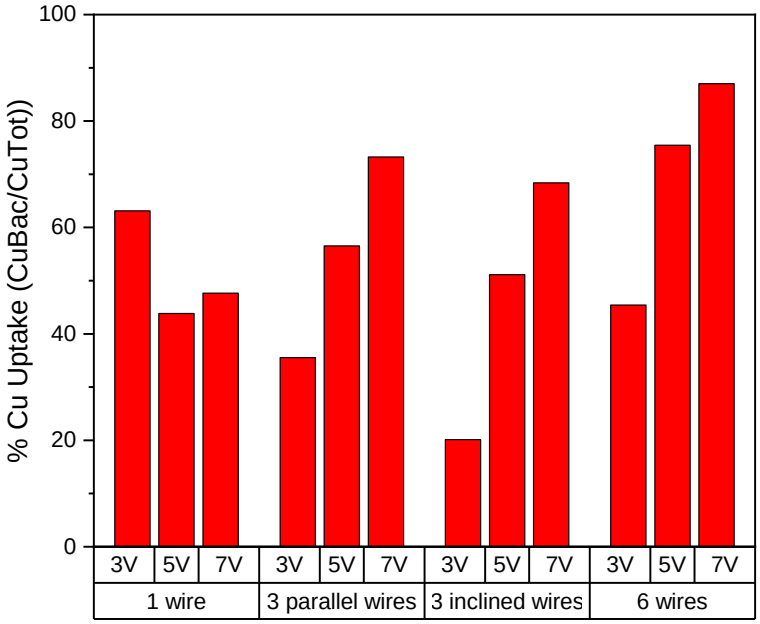

Figure 4.4: Percentage copper uptake (Cu_{bac}/Cu_{tot}) for different anode configurations at 3, 5 and 7 V, treating synthetic water at 150 ml/min.

As is seen in Figure 4.4, in 3 out of the 4 configurations, the percentage of the total copper taken up by the bacteria increased with increase in the voltage. This may be due to the stronger electric field varying the permeability of the cell membrane, which allows more copper to enter the bacterial cells, which in turn increases the disinfection efficiency of the CECIC system.

The disagreement of the 1 wire configuration with this trend may be due to experimental errors; the filtration of those samples was carried out 1 day later, while the effluents from the rest of the configurations were filtered 3-4 hrs after collection (shortly after plating).

4.3 Effect of Flow Rate on Scaled-up CECIC

These experiments were carried out to examine the effect of change in flow rates on the disinfection efficiency of the system. Keeping the baseline of 3 V, 150 ml/min as the reference point, the range of flow rates was set from 100 ml/min (HRT 54 s) to 250 ml/min (HRT 21.6 s) in steps of 50 ml/min so as to provide enough variation in the HRT while remaining within the limitations of the available pump apparatus.

As can be seen in Figure 4.5, all the conditions tested resulted in a high disinfection efficiency (>99.9% or 3-log inactivation). However, each configuration showed a different trend, which has been discussed case-by-case.

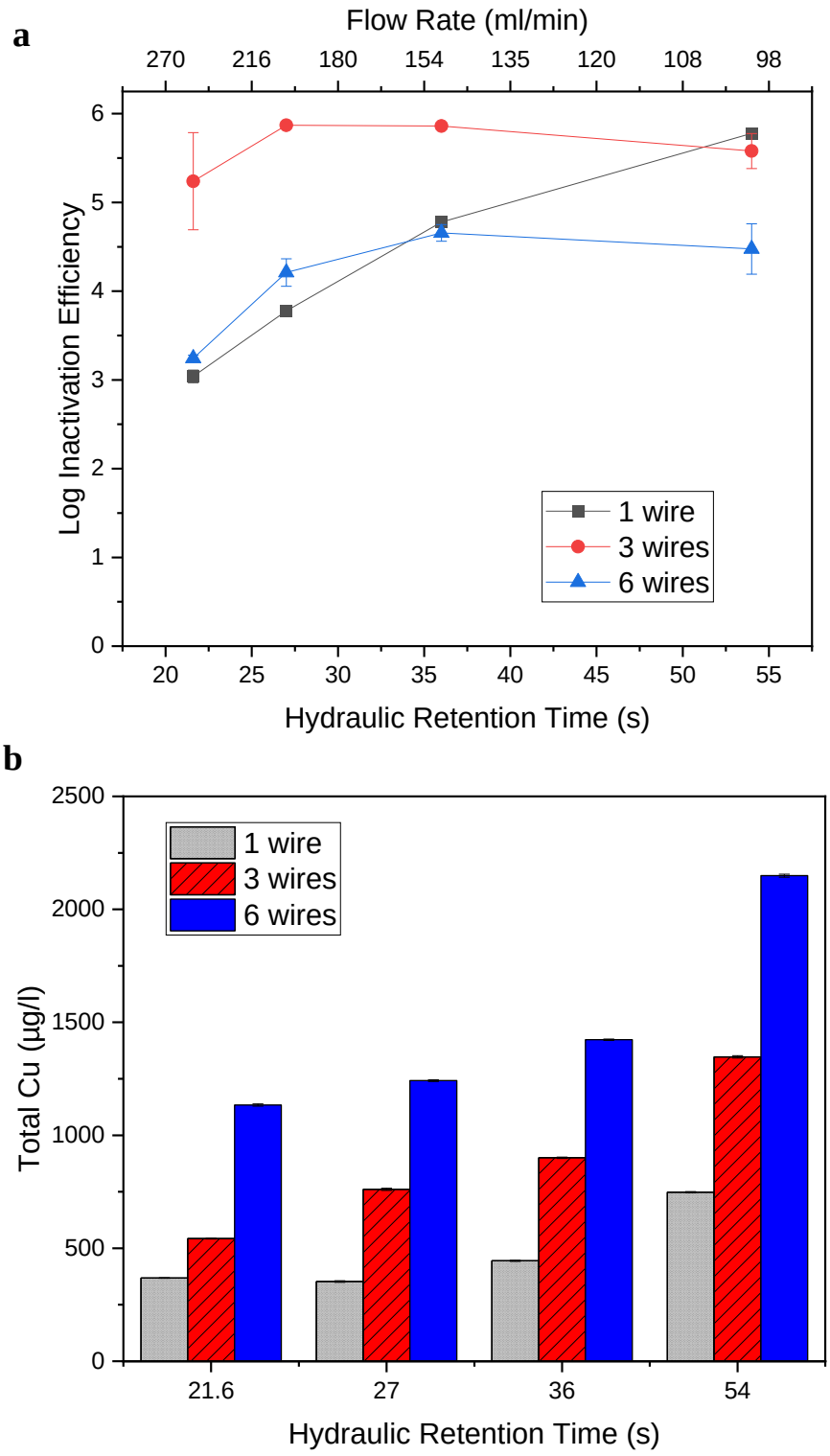

Figure 4.5: (a) LIE and (b) total copper for configurations with 1, 3 and 6 wires, at 250, 200, 150 and 100 ml/min, treating synthetic water at 3 V.

Since copper concentration plays a major role in inactivation of bacteria, insights can be gained on the effect of the electric field and other factors by comparing points with similar copper concentrations, or points where the LIE is higher in spite of lower copper concentrations. At these points, differences in the disinfection efficiency must be due to factors other than copper concentration, such as the electric field effect.

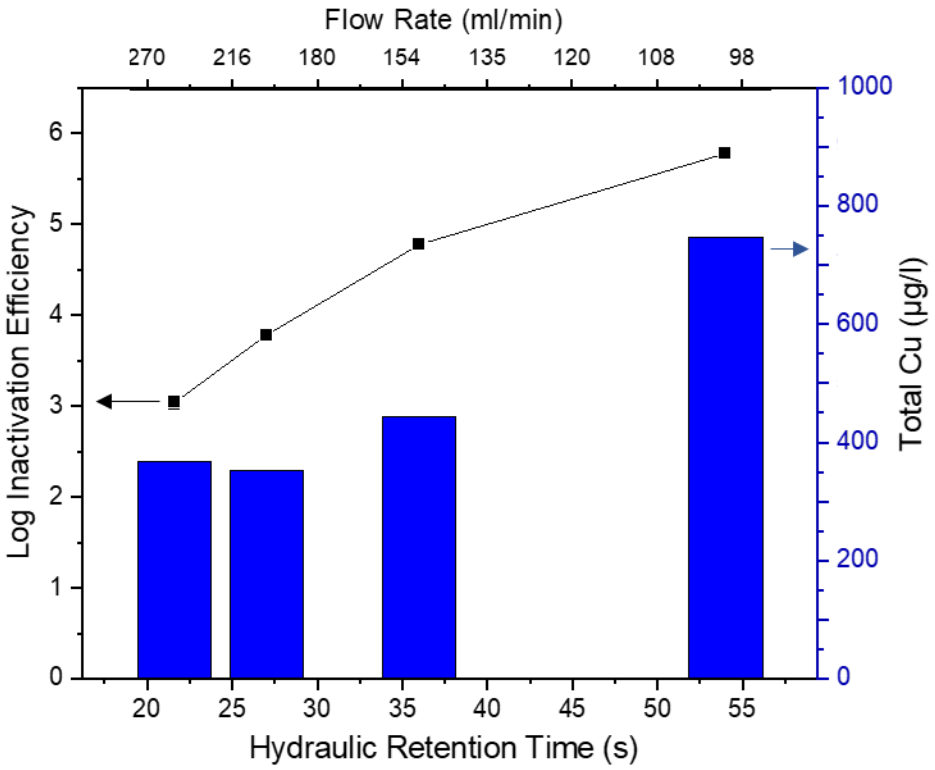

Figure 4.6: Performance of 1-wire configuration at 3 V and flow rates of 250, 200, 150, and 100 ml/min.

For the 1-wire configuration, the LIE increases with increasing HRT, as seen in Figure 4.6. This is especially notable in the case of the first 3 data points, wherein the copper concentration remains in the 350-450 µg/l range but LIE increases from 3.04 to 4.78. This indicates that for the electric field effect plays an important role in this case, with longer exposure to the field leading

to higher disinfection efficiency. Also, this configuration leads to an LIE of 5.78 for a copper concentration of 747 µg/l, which is well within the EPA limit.

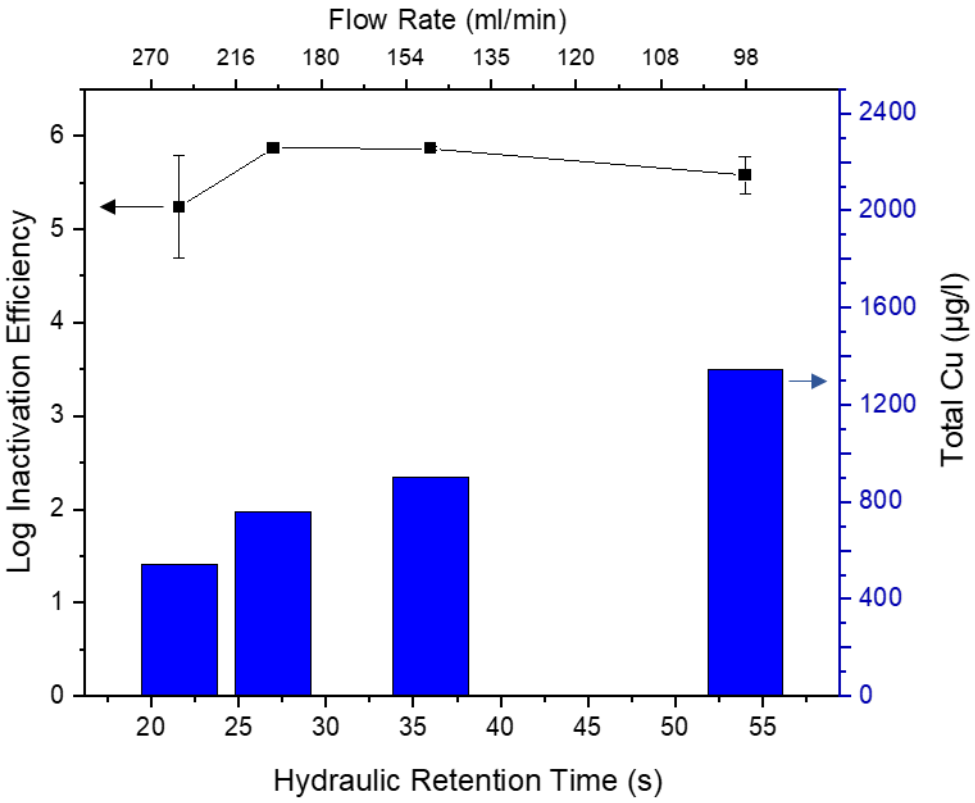

Figure 4.7: Performance of 3-wire configuration at 3 V and flow rates of 250, 200, 150 and 100 ml/min.

For the 3-wire configuration, the LIE is very high and varies only slightly with HRT, remaining in the 5.2 to 5.9-log range, as seen in Figure 4.7. One possible reason for this is experimental: the LIE is close to the upper detection limit even at the lowest value for this experiment (5.2-log), so it cannot go much higher even if increased HRT leads to better disinfection. In that case, a modified experiment may be required to measure the effect of HRT on this configuration. However, there is reason to believe that the results may not be different even if higher inactivation could be measured. As is seen in the constant-copper experiments later in this

chapter, the influence of the electric field strength is stronger than the influence of changes in HRT. Hence, if the electric field in this case is already strong enough to produce very high inactivation, variations in HRT may not affect the disinfection efficiency noticeably.

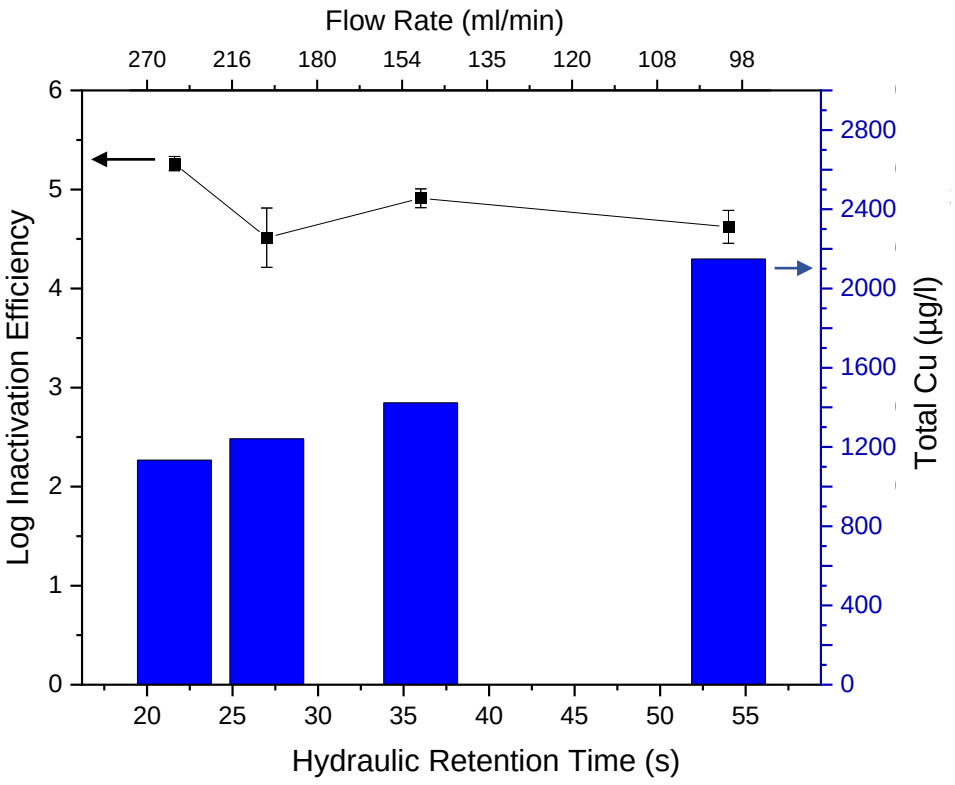

Figure 4.8: Performance of 6-wire configuration at 3 V and flow rates of 250, 200, 150 and 100 ml/min.

Figure 4.8 shows that, for the 6-wire configuration, the LIE is high at all HRTs, but decreases slightly with increasing HRT. This is anomalous, especially since copper concentration increases significantly with increasing HRT. However, the range of LIE values (4.5 - 5.3) is quite narrow, and these differences may have been caused by experimental (equipment) errors.

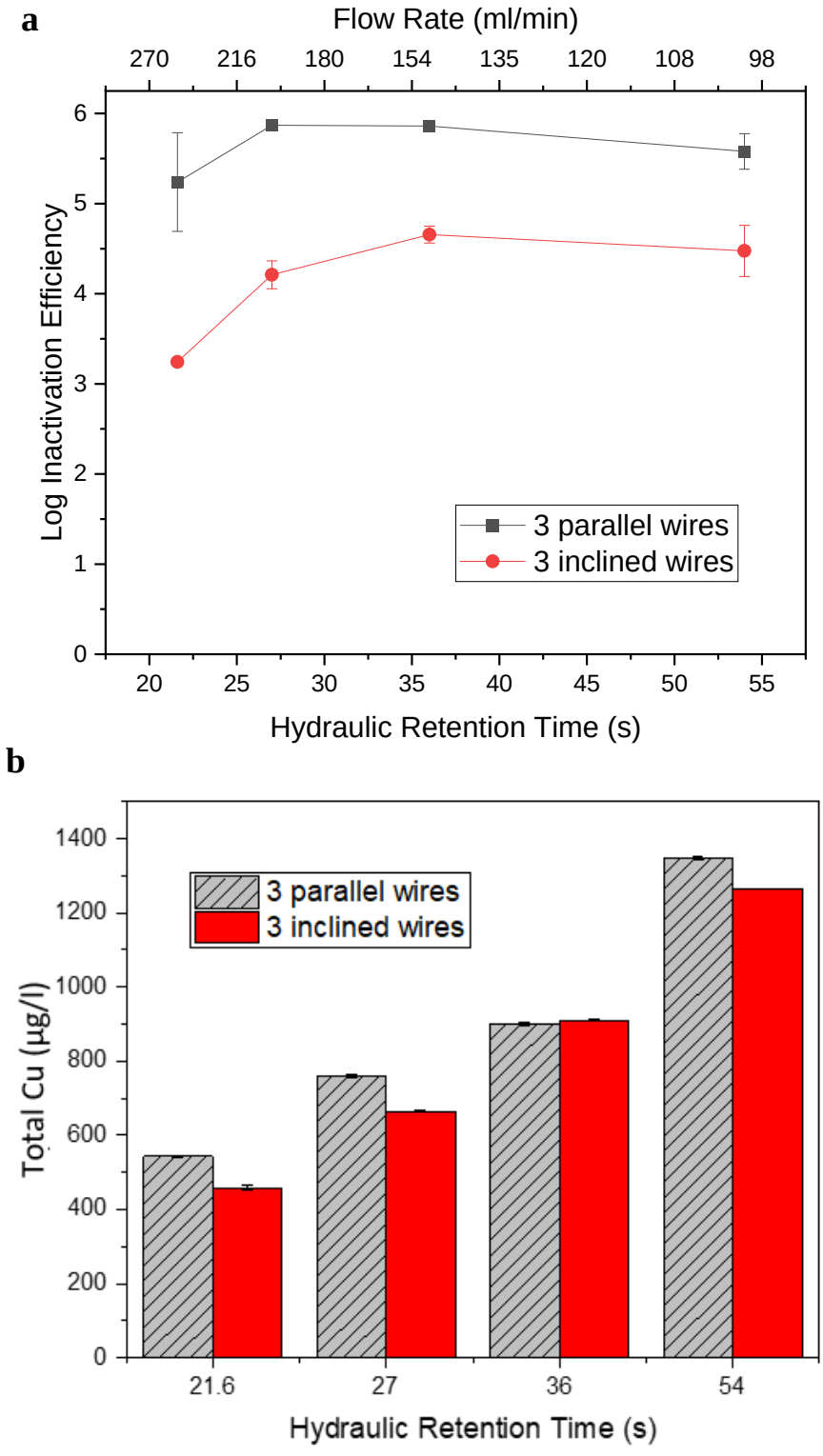

Figure 4.9: (a) LIE and (b) total copper for configurations with 3 straight wires and 3 inclined wires, at 250, 200, 150 and 100, treating synthetic water at 3 V.

In the flow rate response experiments, as in the voltage response experiments, the 3 straight wire configuration performs better than the 3 inclined wire configuration even as both release similar quantities of copper at each flow rate setting. This data, represented in Figure 4.9, corroborates the conclusion that inclining the wires does not improve the disinfection efficiency. One possible reason for this is that the average distance between the anode and cathode is larger in the case of the inclined wires, as a result of which the electric field may be less concentrated at the surface of the wires.

4.4 Effect of Electric Field on Scaled-up CECIC

To ascertain that the electric field, which was proven to play a role in the smaller reactor (Zhou et al, 2020B), also assists with disinfection in the scaled-up reactor, experiments were conducted wherein the current and flow rate were increased proportionately so as to maintain the same copper concentration while increasing the voltage applied. The results of these experiments are shown in Figure 4.10.

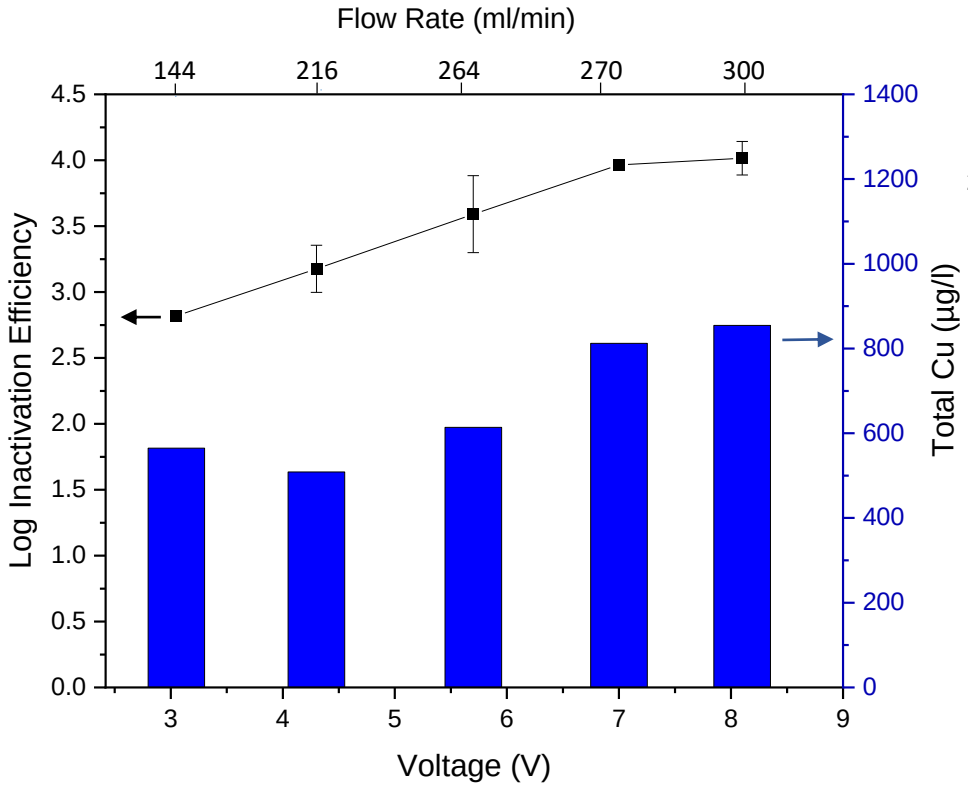

Figure 4.10: LIE and total copper for 1-wire configuration run in constant-copper mode at 4, 6, 8, 10 and 12 mA, with flow rate increased proportionately to maintain constant copper.

Due to instrument errors in the peristaltic pump (actual flow rates deviated significantly from set flow rates at values set above 375 ml/min), the effluent at 7 and 8.1 V contained higher copper values than intended and were not comparable the other 3 data points, as can be seen in Figure 4.10. But comparing between the 3.0, 4.3 and 5.7 V data points, wherein copper concentrations were successfully controlled as intended, it was seen that disinfection efficiency increased with increase in voltage. This effect is notable since the flow rates were also higher at the higher voltage, i.e. the HRT was lower. Hence it can be concluded that the stronger electric field leads to better inactivation of bacteria in spite of the bacteria being exposed to it for a shorter time than in the case of the weaker electric field.

4.5 Effect of Real Water Matrix on Scaled-up CECIC

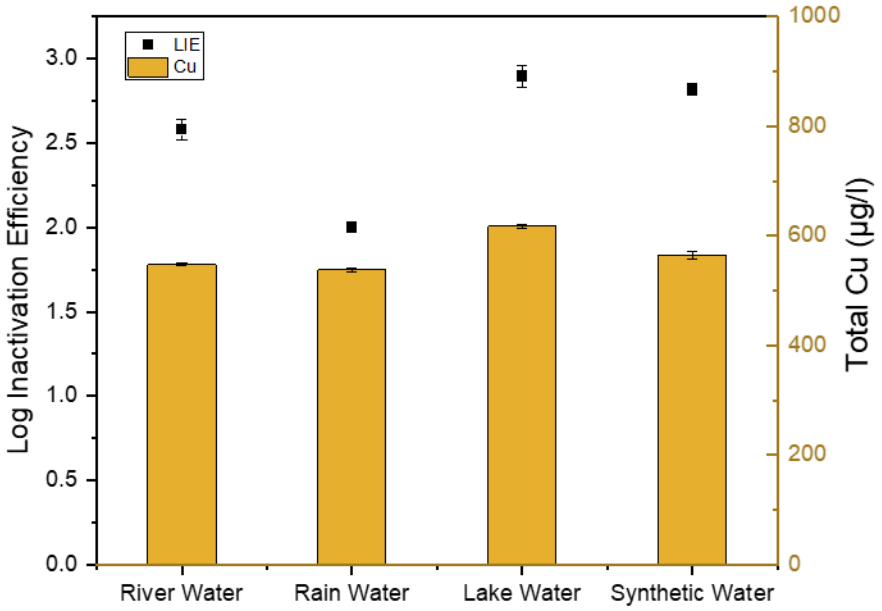

Figure 4.11: LIE and total copper for river water, rain water, lake water, and synthetic water treated at 4 mA and 150 ml/min.

The scaled-up CECIC was run with rainwater (pH 6.23; conductivity 59.18 µS/cm), river water (pH 8.87; conductivity 90.72 µS/cm) and lake water (pH 9.02; conductivity 61.23 µS/cm) at a constant current of 4 mA and flow rate of 150 ml/min. This resulted in a voltage of 2.07 V with the river water sample, and higher voltages of 4.26 and 4.45 for rain water and lake water respectively, due to their lower conductivities. As can be seen in Figure 4.11, all copper concentrations were between 530 and 620 µg/l and >2-log inactivation (>99% disinfection) was achieved with all samples. In spite of this higher voltage, the LIE was lower for rain water than for river water, which requires investigation. Compared to the synthetic water control (pH 6.42; conductivity 96.23 µS/cm), both real water effluents showed lower LIE values even though their total Cu and bacterial Cu values were similar. This is likely due to interference from other dissolved substances in the water matrix, which requires further study.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The results obtained here have shown that, as CECIC is scaled up to larger pipes, a cell design with multiple wires merits consideration. In the few cases where performance could be compared independent of copper concentration, the 3 wire configuration seemed to perform the best. However, data on this is scarce and requires further investigation.

The results did not provide enough evidence to suggest that twisting the wires improves performance. To the contrary, they suggest that it may reduce the disinfection efficiency. This may be due to the greater average distance between the anode and cathode in the case of the twisted configuration, which may reduce the strength of the electric field closer to the middle section of the cell, where the anode wires are closer to the axis of the cell. Thus any advantage gained by placing the wire at an angle to the flow, such as mixing or increased contact with bacteria, is likely lost due to the weaker electric field effect.

The results also demonstrate that the electric field does play an important role in the disinfection performance of the scaled-up cell. After controlling for total copper release, the higher voltage was found to produce a higher LIE. The likely reason for this is the increased permeability of the bacterial cell membrane under the stronger electric field, making it more susceptible to the bactericidal effects of copper.

Among the various combinations of parameters and configurations tested, the 3-wire configuration operated at 3 V and 200 ml/min showed the best performance within EPA discharge limits, producing 5.9-log inactivation while releasing 761 µg/l Cu. This demonstrates that the

scaled-up CECIC can achieve high disinfection efficiency in waters with real-world levels of conductivity. This performance is noteworthy since it represents successful operation with a step-up in cell size, flow rate, and water conductivity compared to previous tests of the smaller CECIC.

The performance of the scaled-up CECIC on real water samples was found to be lower than that on synthetic water, possibly due to interference of dissolved substances in the water matrix. Further investigation is required to determine the cause of that interference, and to explore solutions including coupling of CECIC with other treatment technologies such as ozonation or LEEFT. Developing a process model will be helpful in this regard, allowing the simulation of disinfection efficiency under various conditions, which in turn can guide system design. To begin with, the distribution of copper ions and movement of bacterial cells within the CECIC can be simulated along the lines of work by Zhou et. al (2019). This can be followed by disinfection simulations to screen more CECIC configurations and operational parameter variations in silico and then test the most promising ones in the lab.

Also, these tests were limited to *E. coli*, and further testing with a wider range of model microorganisms, such as viruses (MS-2 coliphage) and gram-positive bacteria (*B. subtilis*), may be required as a stepping-stone to real-world applications. Future studies should also include a wider range of natural waters, such as groundwater or surface waters with higher conductivity, which may present a challenge to CECIC disinfection. Lastly, design modifications may be required in the process of further scaling-up the system in order to accommodate the 2-hour residence time needed for the copper disinfection to take effect at the levels recorded in these tests. Nonetheless, the scaled-up CECIC successfully inactivated over 99% of the *E. coli* in both river and rainwater samples, showing promise for pilot tests and eventual real-world applications.

APPENDIX: EXPERIMENTAL DATA

Symbols in the table:

W: configuration (1 – 1 coaxial wire; 3p – 3 parallel wires; 3i – 3 inclined wires; 6 – 6 parallel wires)

C: conductivity (µS/cm)

IB: Influent bacteria (*10^6 CFU /ml)

LIE: log inactivation efficiency

eLIE: LIE error

I: current (mA)

V: voltage (V)

F: flow rate (ml/min)

HRT: hydraulic retention time (s)

CuT: total copper concentration (µg/l)

eCuT: error in total copper concentration (µg/l)

CuD: dissolved copper concentration (µg/l)

eCuD: error in dissolved copper concentration (µg/l)

CuB: bacterial copper concentration (µg/l)

eCuB: error in bacterial copper concentration (µg/l)

U: uptake of copper concentration (%)

CuTh: theoretical copper concentration (µg/l)

ηCu: Coulombic Efficiency of Copper release (%)

BD: Below Detection limit

NA: Not Available

Table A1: Experimental data

W	C	pH	IB	LIE	eLIE	I	V	F	HRT	CuT	eCuT	CuD	eCuD	CuB	eCUB	U	CuTh	ηCu
1	95.85	6.6	192	0.28	0.00	0.34	0.5	150	36	BD	BD	BD	BD	BD	BD	BD	44.77	0.00
1	95.85	6.6	192	2.28	0.00	0.75	1	150	36	BD	BD	BD	BD	BD	BD	BD	98.77	0.00
1	95.85	6.6	192	3.40	0.06	3.9	3	150	36	459.7	8.2	169.5	2.9	290.2	11.1	63.13	513.59	89.51
1	95.85	6.6	192	3.63	0.11	7.7	5	150	36	976.6	1.4	548.5	2.58	428.1	3.98	43.84	1014.01	96.31
1	95.85	6.6	192	5.90	0.31	11.8	7	150	36	1722	0.25	901.4	2.66	820.6	2.91	47.65	1553.93	110.82
3 p	95.16	6.12	38	0.32	0.03	0.42	0.5	150	36	BD	BD	BD	BD	BD	BD	BD	55.31	0.00
3 p	95.16	6.12	38	0.74	0.09	1.19	1	150	36	111.9	5.01	32.44	4.99	BD	BD	BD	156.71	71.41
3 p	95.16	6.12	38	4.63	0.00	6.7	3	150	36	707.8	3.05	456.2	0.51	251.6	3.56	35.55	882.32	80.22
3 p	95.16	6.12	38	5.60	0.02	12.8	5	150	36	2111	7.38	917.7	0.89	1193.3	8.27	56.53	1685.62	125.24
3 p	95.16	6.12	38	5.61	0.02	19.3	7	150	36	3031	6.21	810.7	2.08	2220.3	8.29	73.25	2541.60	119.26
3 i	92.21	6.11	30	0.47	0.01	0.6	0.5	150	36	BD	BD	BD	BD	BD	BD	BD	79.01	0.00
3 i	92.21	6.11	30	0.76	0.11	1.42	1	150	36	104	6.84	16.35	3.15	BD	BD	BD	187.00	55.62
3 i	92.21	6.11	30	4.33	0.24	6.45	3	150	36	939.4	6.78	750.3	4.61	189.1	11.39	20.13	849.39	110.60
3 i	92.21	6.11	30	4.76	0.08	11.7	5	150	36	1849	5.62	903.5	5.76	945.5	11.38	51.14	1540.76	120.01
3 i	92.21	6.11	30	5.52	0.00	17.7	7	150	36	2311	1.62	730.7	2.83	1580.3	4.45	68.38	2330.90	99.15
6	95.35	6.03	43	0.44	0.07	1.02	0.5	150	36	80.41	1.19	38.41	2.38	42	3.57	52.23	134.32	59.86
6	95.35	6.03	43	2.19	0.08	2.25	1	150	36	284.7	2.67	175	2.96	109.7	5.63	38.53	296.30	96.08
6	95.35	6.03	43	5.27	0.08	11.7	3	150	36	1605	5.32	876.1	1.91	728.9	7.23	45.41	1540.76	104.17
6	95.35	6.03	43	5.55	0.15	22.01	5	150	36	3092	9.63	758.8	3.27	2333.2	12.9	75.46	2898.48	106.68

W	C	pH	IB	LIE	eLIE	I	V	F	HRT	CuT	eCuT	CuD	eCuD	CuB	eCUB	U	CuTh	ηCu
6	95.35	6.03	43	5.66	0.02	35	7	150	36	4383	10.08	569.5	3.36	3813.5	13.44	87.01	4609.12	95.09
1	95.05	5.98	54	3.04	0.07	3.55	3	250	21.6	368.1	1.36	274.8	1.89	93.3	3.25	25.35	280.50	131.23
1	95.05	5.98	54	3.78	0.00	3.8	3	200	27	352.8	3.58	251.3	5.74	101.5	9.32	28.77	375.31	94.00
1	95.05	5.98	54	4.78	0.00	3.9	3	150	36	444.4	2.23	319.3	1.55	125.1	3.78	28.15	513.59	86.53
1	95.05	5.98	54	5.78	0.00	4.22	3	100	54	747.8	2.74	527.6	3.94	220.2	6.68	29.45	833.59	89.71
1	95.05	5.98	54	4.33	0.23	4.33	3	50	108	1102	5.59	247	5.86	855	11.45	77.59	1710.64	64.42
3 p	94.46	6.07	69	5.24	0.55	6.4	3	250	21.6	542.8	1.88	365.7	2.97	177.1	4.85	32.63	505.69	107.34
3 p	94.46	6.07	69	5.87	0.02	6.7	3	200	27	760.9	4.98	494.2	5.15	266.7	10.13	35.05	661.74	114.99
3 p	94.46	6.07	69	5.86	0.02	6.95	3	150	36	900.5	3.12	480.9	3.33	419.6	6.45	46.60	915.24	98.39
3 p	94.46	6.07	69	5.58	0.20	7.05	3	100	54	1347	5.28	608	5.19	739	10.47	54.86	1392.61	96.72
3 p	94.46	6.07	69	4.54	0.30	6.82	3	50	108	2206	5.34	127.1	2	2078.9	7.34	94.24	2694.36	81.87
3 i	94.06	6.17	118	3.24	0.03	5.86	3	250	21.6	459	5.62	189.6	3.67	269.4	9.29	58.69	463.02	99.13
3 i	94.06	6.17	118	4.21	0.15	6.25	3	200	27	665	3.26	271.8	0.37	393.2	3.63	59.13	617.29	107.73
3 i	94.06	6.17	118	4.66	0.09	6.35	3	150	36	910.6	3.42	333	6.37	577.6	9.79	63.43	836.23	108.89
3 i	94.06	6.17	118	4.48	0.28	6.38	3	100	54	1265	1.21	383.9	2.01	881.1	3.22	69.65	1260.26	100.38
3 i	94.06	6.17	118	4.44	0.05	6.1	3	50	108	2428	4.81	142	4.07	2286	8.88	94.15	2409.91	100.75
6	95.36	6.26	90	5.26	0.07	11.4	3	250	21.6	1134	5.04	548.5	2.45	585.5	7.49	51.63	900.75	125.89
6	95.36	6.26	90	4.51	0.30	11.35	3	200	27	1242	3.7	296.8	2.46	945.2	6.16	76.10	1121.00	110.79
6	95.36	6.26	90	4.91	0.10	10.98	3	150	36	1423	3.04	130.2	2.18	1292.8	5.22	90.85	1445.95	98.41
6	95.36	6.26	90	4.62	0.17	11.15	3	100	54	2149	6.71	757.1	3.03	1391.9	9.74	64.77	2202.50	97.57
6	94.81	6.26	213	4.03	0.05	11.8	3	50	108	4317	8.84	373.2	3.87	3943.8	12.71	91.36	4661.79	92.60
1	96.23	6.42	109	2.82	0.03	4	3.0	144	37.5	564.8	7.34	198.2	3.27	366.6	10.61	64.91	548.70	102.93
1	96.23	6.42	109	3.18	0.18	6	4.3	216	25	508.6	0.94	221.4	4.92	287.2	5.86	56.47	548.70	92.69
1	96.23	6.42	109	3.59	0.29	8	5.7	264	20.4	614	3.39	239.8	3.05	374.2	6.44	60.94	598.59	102.57
1	96.23	6.42	109	3.96	0.01	10	7	270	20	812.1	3.65	397.8	3.47	414.3	7.12	51.02	731.61	111.00
1	96.23	6.42	109	4.02	0.13	12	8.1	300	18	854.6	3.17	404.6	1.84	450	5.01	52.66	790.13	108.16
1	90.72 river water	8.87	91	2.58	0.06	4	2.07	150	36	547.7	2.06	215.3	2	332.4	4.06	60.69	526.76	103.97
1	59.18 rainwater	6.23	92	2	0.02	4	4.26	150	36	538	3.77	214.6	2.16	323.4	5.93	60.11	526.76	102.13
1	61.23 lake water	9.02	68	2.89	0.07	4	4.45	150	36	617.8	3.63	NA	NA	NA	NA	NA	526.76	117.28

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